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54 Title: A method of determining the concentration of additives in galvanic metal deposition baths analytically

57 The invention concerns methods of determining, separately and analytically, the concentrations of brightening and leveling additives in galvanic metal deposition baths, in which the potential of the working electrode is varied cyclically against the reference electrode between potential limits in an electrochemical arrangement with working, counter and reference electrodes in a measurement cell. To determine the concentrations, either first the concentration of leveling additive is found by a titration method and then the concentration of brightening additive is derived from a predetermined calibration matrix, or the concentration of brightening additive is found first by a titration method and then the concentration of leveling additive is derived from the calibration matrix.

Description

The invention concerns a process for determining, separately and analytically, the concentrations of brightening and leveling additives in galvanic metal deposition baths, especially copper deposition baths.

Galvanic metal deposition baths are usually used to treat metallic and electrically nonconductive materials. For example, copper deposition baths are used to form tracks on printed circuit boards and electrical connecting elements between several layers of the board by copper-plating bore-hole walls in the printed circuit boards. Galvanic metal deposition baths are also used to produce decorative surface layers, for example as a basic layer of chrome end layers made of steel parts.

Galvanic copper baths contain mainly inorganic components: besides a source of copper ions, for example copper sulfate or another copper salt, they contain materials to increase the electrical conductivity of the bath, for example sulfuric acid, methane sulfonic acid or fluoroboric acid. Baths containing sulfuric acid and copper sulfate also contain chlorides in small concentrations.

In addition to the components mentioned, there are generally other additives in the bath to help adjust special properties of the metal layers deposited from the baths. For example, it is almost always desired that the metal layers deposited be high-gloss and that uneven areas in the basic material being coated be leveled to be able to deposit a very level copper coating. Also, in most cases, the copper layers must have high enough ductility and tensile strength. The baths contain brightening and leveling additives for this. These are generally organic compounds that affect the deposition mechanisms. The usual organic sulfur compounds, for example sulfides and disulfides, are used as brightening compounds. Glycolic ether is used as a leveling additive, for example. But polymer materials can also be used. While the brightening additives have the effect of promoting deposition, the leveling substances substantially inhibit deposition, so that relatively high excess voltage must be applied during deposition. Therefore, the latter substances apparently promote the formation of mini-crystals in the layer, resulting in fine-grained layers.

It turns out that the concentrations of these additives in the galvanic copper baths can be followed only with very expensive methods. For example, in "Modern Analysis of Acidic Copper Baths" by B. Bressel, W. Dahms, M. Wolter and M. Guendel in Galvanotechnik, Volume 75 (1984), pages 1488 to 1493, it says that high-performance liquid chromatography can be used as an analytical method to determine the concentration of brightening components. It also turns out that the concentration of these additives can change relatively abruptly in short periods of time.

Another method proposed is cyclic voltammetry. This is an electrochemical measurement method. It is described that to perform cyclic voltammetry, a three-electrode arrangement with a potentiostatic measurement arrangement consisting of a rotating working electrode, a counter electrode made of platinum and a reference electrode (silver/silver chloride electrode) can be used. A cyclic voltammogram is obtained by putting the electrodes in contact with the bath sample being studied, varying the potential of the working electrode continually and cyclically between certain potential limits and measuring the resultant current flow. Copper is therefore deposited under 0.1 V (volts) in relation to the potential of the silver/silver chloride electrode (vs. Ag/AgCl) on the working electrode and then removed again in the potential range from +100 mv to +400 mV vs. Ag/AgCl. This produces an anode dissolution peak, whose surface is proportional to the amount of copper deposited beforehand. This surface is used to analyze the additive content. The so-called addition method is used to determine the brightening additive with this surface, according to the data in this publication;e after initial analysis of the bath by this method, successive small increments are added to a calibration solution that contains only the brightening components, and each time the peak area is determined. After graphic evaluation, calibration lines are obtained, from which the content of these additives being determined can be obtained by extrapolation on the abscissa.

As shown before, the concentrations of brightening and leveling additives in the deposition bath frequently change relatively abruptly within short intervals of time, so the bath must be analyzed at short intervals of time.

However, typically, galvanic copper baths have thus far been monitored only by taking bath samples out of the bath manually once or twice a day and studying them for the content of the above-mentioned components. But this method of control has proven insufficient for process assurance due to the risk that the concentrations of additives can change abruptly.

EP 0 154 705 A2 proposes a method of full automatic control of the galvanic deposition of copper coatings from acidic copper baths. This method also uses the cyclic voltammetry method with a potentiostatic three-electrode arrangement with a working electrode designed as a rotating disk electrode. The height of the dissolution peak is measured in this case for evaluation. Periodically determining the peak height over and over again with a bath solution fed continually into the measurement cell allows the bath to be monitored continually. It is specified that the peak height is constantly compared to a set value, and if it falls below said value, brightening additives are added to the bath. No instructions are given on continually monitoring the leveling additives.

However, this method is sensitive, since the device necessary for analysis is complex. Such automatic analysis machines must also supply concrete results over a long period of time with no problem under crude

production conditions. A method of fully automatic analysis of just the brightening, but not the leveling component of the bath is also described.

The problem is also that rotating disk electrodes made of platinum must be used for the area surrounding the additives when using cyclic voltammetry methods that result from material transport in the measurement solution near the electrode. The method is characterized by a high calibration expense, which must be repeated for each analysis.

The problem of this invention is therefore to prevent the disadvantages of the known method and especially to find a method of separately analytically determining concentrations of brightening and leveling additives in galvanic metal deposition baths. The method should be simple to perform and should be able to result in low calibration expense for measuring the individual components of the bath.

This problem is solved by the method in Claims 1 and 3. Preferred embodiments of the invention are given in the subclaims.

To determine the concentrations of brightening and leveling additives in galvanic metal deposition baths, an electrochemical three-electrode arrangement with working, counter and reference electrodes is used in a measurement cell with a potentiostatic arrangement, in which the potential of the working electrode is varied cyclically against the reference electrode between potential limits, and metal is deposited on the working electrode and is then dissolved again afterward. Since the amount of metal deposited and then dissolved again afterward depends on the concentrations of the additives being determined, this method can be used successfully to analyze them.

To create a safe, easy working method, especially one without a big expense for calibration, the method in the invention, in a separate calibration method, first determines the amount of metal deposited on the working electrode and dissolved again after deposition of various bath compositions containing different contents of brightening and leveling additives. They contain triple values (amount of metal, concentration of brightening additive and concentration of leveling additive), which together form a calibration matrix. The calibration matrix can be shown, for example in a 3D graph, in which the amount of metal deposited or dissolved again is placed on the ordinate and the concentrations of brightening and leveling additives on the two abscissas.

To determine the concentrations of brightening and leveling additives in a deposition bath, first one of the two concentrations can be determined by the measurement method and then the other by measuring the amount of

metal deposited or dissolved, and it can then be read on the graph. Of course, other types of representation can also be chosen for the correlations between the quantity of metal deposition or dissolution in the concentrations, for example tables in written form or stored on data carriers, as well as in the form of mathematical functions determined by approximation methods, from which the respective concentrations can be determined by simple computing operations.

Basically, there are two measurement methods in the invention:

1. The metal deposition bath is transferred into a measurement cell. Then the concentration of leveling additive is determined by a titration method, by determining the amount of metal deposited on the working electrode or the amount of metal dissolved again after deposition. Then the concentration of brightening additive is derived from the predetermined concentration of leveling additive and the values that were found by the separate calibration method used before.

The concentration of leveling additive in the metal deposition bath can be found by a measurement method titrating a metal deposition bath without additives in two titration cycles

- once with the metal deposition bath being analyzed, for example the production bath, and
- once with a standard solution containing the leveling additive in a known concentration

and then the concentration of leveling additive is calculated using the equation:

$$X_{EZ} = C_{EZ}\, a_u / a_s$$

where

X_{EZ} = the concentration of leveling additive in the metal deposition bath being analyzed,

C_{EZ} = the known concentration of leveling additive in the standard solution

a_u = the rise in the titration analysis curve (amount of metal deposited or dissolved again after deposition as a function of the volume of the metal deposition bath being analyzed that was added during titration) and

a_s = the rise in the standard titration curve (amount of metal deposited or dissolved again after deposition as a function of the volume of standard solution added during titration).

Standard solution in this case is understood as a solution that contains the leveling additive in the known

concentration, but not the brightening additive, for example a solution that contains, in addition to the inorganic components of the metal deposition bath, for example in the case of a standard copper bath, copper sulfate, sulfuric acid and chloride in water, as other components, only the leveling additives.

2. In the second alternative in the invention, the metal deposition bath is also transferred into the measurement cell. Then the concentration of brightening additive is found by a titration method, wherein the amount of metal deposited on the working electrode or the metal dissolved again after deposition is found in each titration step. Then, the concentration of leveling additive is derived from the concentration of brightening additive already found and the values found using the separate calibration method used before.

The concentration of brightening additive can be determined by titrating the metal deposition bath being analyzed with a standard solution containing the brightening additive in a known concentration and deriving the concentration from the abscissa section of the titration curve obtained (amount of metal deposited or dissolved again after deposition as a function of the volume of the standard bath added during titration). Standard solution in this case is understood as a solution that contains the brightening additive, but not the leveling additive, for example a solution that contains, besides the inorganic components of the metal deposition bath, as other components, only the brightening additive.

With the method in the invention, it is possible to determine the concentration of both the brightening and leveling additives in the metal deposition bath separately, without having to perform several analyses. This technique is especially suitable for continual process monitoring. Since only one of the two components is determined analytically in a measurement method, for example in a so-called on-line operation, and the other is determined from the calibration matrix measured beforehand, the analysis expense is reduced to a small amount compared to conventional techniques. Thus, fewer complex apparatuses are needed to perform these types of analyses, so the whole system is less prone to problems. The calibration matrix only hs to be set up once before performing the first analysis of a metal deposition bath.

The calibration matrix can be set up in the following way:

a. Make metal deposition baths with known concentrations of brightening and leveling additives.
b. Determine the quantity of metal deposited on the working electrode or dissolved again after deposition with each of the metal deposition baths made.
c. Assign measured values for the amount of metal deposited on the working electrode or dissolved again

after deposition to the predetermined pairs of concentration values for the brightening and leveling additives.

The common triple-electrode arrangement used in electrochemistry that has a working electrode, a counter electrode and a reference electrode is used for the method. During the analysis operation, the voltage between the working electrode and the reference electrode is firmly set, and the current flowing between the working electrode and the counter electrode is then measured. The electrodes used for the working electrode and the counter electrode are typically high-quality metal, preferably platinum. To prevent adverse effects that cause uncontrollable material transport to the surface of the electrode, the working electrode is usually designed as a rotating disk electrode with a rotation speed of approximately 1000 rpm. As the reference electrode, a silver/silver chloride electrode can be used. Kalornel electrodes can also be used as reference electrodes.

To find the amount of metal deposited on the working electrode or dissolved again after deposition, the voltage between the working electrode and the reference electrode is varied linearly with time, for example between –0.25 V and +1.0 V vs. Ag/AgCl. In the potential range under 0 V vs. Ag/AgCl, metal is deposited on the working electrode. This is expressed in a negative deposition current. If the potential of the working electrode is then changed to positive values, this metal is dissolved again in the potential range from 0 to +0.3 V vs. Ag/AgCl. This results in a positive current (stripping peak). The negative deposition current should be largely equal to the positive stripping current.

One way of finding the amount of metal deposited or the amount of metal dissolved (or the charge) is to record the current during deposition and/or subsequent dissolution and to integrate them over time, since the amount of charge that flows is determined this way.

In the above-mentioned titration methods of setting up the calibration matrix and analyzing the brightening and leveling additives, therefore, the amount of metal deposited or dissolved again after deposition is expressed by the amount of charge that is found passing through the respective potential range. Therefore, instead of the amount of metal deposited or dissolved in the corresponding representations (graphic, table form, written or stored on data carriers), the amount of charge can also be used as a measured value. Of course, the amount of metal can also be used after conversion.

This method can also be used especially to determine the calibration matrix. For this, the amounts of metal deposited and/or dissolved again (or the amounts of charge) are assigned to the corresponding pairs of concentration values of brightening and leveling additives set beforehand in a metal deposition bath and recorded.

The concentration of brightening additive can be determined separately by a titration method. For this, first preferably a certain amount of leveling additive is added to the metal deposition bath being analyzed. After that, the standard bath containing a known concentration of brightening additive is titrated. The amount of metal deposited or dissolved again is found to rise linearly with the titration volume. Extrapolating this straight line on the abscissa gives the content of brightening additive in the solution.

The concentration of leveling additive can be found by another titration method. For this, two titrations are done with a metal deposition bath without additives (basic bath: for example, a basic copper bath, consisting of copper sulfate, sulfuric acid and chloride in water):

- once with the metal deposition bath being analyzed,
- once with a standard solution containing a known concentration of leveling additive.

During titration, the amount of metal deposited or dissolved again is found. The amount of metal basically decreases linearly as the titration volume increases. The concentration of leveling additive is calculated from these titration lines using the equation above.

Instead of a rotating disk electrode, a microelectrode can also be used as the working electrode. Microelectrodes eliminate the disadvantages inherent in the usual disk electrodes, which result in insufficient material transport on the electrode surface. Since microelectrodes do not have to be designed as rotating electrodes, the measurement arrangement can be built more simply and less prone to maintenance and repair.

As the microelectrode, for example, the cross section of a high-quality metal wire embedded in an insulating material with a diameter of maximum 50 μm, for example 10 to 50 μm, can be used. As the high-quality metal wire, a platinum wire is preferably used. To make it, it can be embedded in a synthetic resin or melted into glass, and then the cross section of the wire can be freed, or example by sawing and grinding.

In another method in the invention, the amount of metal deposited on the working electrode or dissolved again can be determined by a direct change in mass using a quartz resonator technique. For this, a quartz resonator coupled to a suitable oscillation excitation circuit with an electrode surface is used as the working electrode. To detect the mass change during deposition or dissolution of the metal, the frequency change during deposition or dissolution is measured, and the amount of metal deposited or dissolved is found from the frequency change by means of a calibration line or from the equation developed by Sauerbrey and the Faraday equation. In this case, the

amount of metal is expressed in the titrations or in the calibration matrix by a frequency shift. For the experimental requirements for direct change in the mass change during metal deposition and/or dissolution, please refer to R. Schumacher in "The Quartz Microbalance: A Novel Approach to the In-Situ Investigation of Interfacial Phenomena at the Solid/Liquid Junction," Angewandte Chemie [Applied Chemistry], Volume 29 (1990), pages 329 to 343, especially pages 330, 331.

The method in the invention is preferably used to find the concentrations of brightening and leveling additives in galvanic copper deposition baths, especially copper baths containing sulfuric acid.

As brightening additives, these baths can contain mainly organic mercapto, sulfide and disulfide compounds, such as 3-(benzthiazolyl-2-thio)-propylsulfonic acid, sodium salt, 3-mercaptopropane-1-sulfonic acid, sodium salt, ethylene dithiopdipropyl sulfonic acid, sodium salt, bis-(p-sulfophenyl)-disulfide, disodium salt, bis-(ω—sulfophenyl)-disulfide, disodium salt, bis-(ω-sulfobutyl)-disulfide, disodium salt, bis-(ω-sulfohydroxypropyl)-disulfide, disodium salt, bis-(ω-sulfopropyl)-disulfide, disodium salt, bis-(ω-sulfopropyl)-sulfide, disodium salt, methyl-(ω-sulfopropyl)-disulfide, disodium salt, methyl-(ω-sulfopropyl)-trisulfide, disodium salt, O-ethyl-dithiocarbonic acid-S-(ω-sulfopropyl)-ester, potassium salt, thioglycolic acid, thiophosphoric acid-O-ethyl-bis-(ω-sulfopropyl)-ester, disodium salt, thiophosphoric acid-tris-(ω-sulfopropyl)-ester, trisodium salt, and cyclic sulfur compounds, such as thiazol.

As leveling additives, inter alia, glycol ether and polymer materials are used, for example carboxymethyl cellulose, nonylphenol-polyglycol ether, octandiol-bis-(polyalkylene glycol ether), octanolpolyalkyleneglycol ether, oleic acid polyglycol ester, polyethylene propylene glycol, polyethylene glycol, polyethylene glycol dimethyl ether, polyoxypropylene glycol, polypropylene glycol, polyvinyl alcohol, stearic acid-polyglycol ester, stearyl alcohol-polyglycol ether, beta-naphtholpolyglycol ether.

The method is suitable for use in continual automated process monitoring. Above all, the analytic method in Claim 3 is simple and requires few analysis steps to perform online monitoring.

Modern automatic analysis machines can be used for this in which the measurement cells needed to titrate the bath samples are filled automatically, refilled after titration, then cleaned and can be refilled. Predetermined steps in the process can also be controlled by automation, for example, titration of the bath samples with a titrating liquid and the electrochemical analyses to be done between individual titrating cycles with current measurement or measurement of the mass change with a quartz resonator. The bath liquid can be circulated in a bypass to the actual

treatment container containing this fluid, and partly run through other liquid lines into the analysis machines. The analysis data obtained is processed in a computer, and the predetermined calibration matrix is also stored in the computer to make it possible to calculate the derived data quickly (content of additives not found experimentally). The concentrations now found are compared to set values. If deviations are found, the dosing pumps with which concentrates of the additive are fed into the bath are checked.

The invention will be explained in greater detail below using the following examples:

Example 1

To find the concentrations of brightening and leveling additives in a galvanic copper bath that contains the following inorganic components:

$CuSO_4 \cdot 5H_2O$	0.3 Mol/liter
Concentrated H_2SO_4	2 Mol/liter
Cl (as NaCl)	50 mg/liter
in water	

First a calibration matrix is set up for the brightening and leveling additives in the bath. The calibration solution used for the brightening additives is the brightening additive CUPRACID®BL (Atotech Deutschland GmbH, Berlin, DE) and the calibration for the leveling additive is the basic leveler CUPRACID® BL . The brightening additive (BA) and the basic leveler (BL) basically contained only the brightening (BA) or leveling (BL) additives.

To set up the calibration matrix, various bath solutions are used that contain the above-mentioned basic composition with inorganic components (copper sulfate, sulfuric acid, sodium chloride) and also the brightening additive and the basic leveler with phased concentrations in ranges from 0 to 3 ml of brightening additive CUPRACID® BL/liter of solution for the brightening additive and 0 to 15 ml of basic leveler CUPRACID® BL/liter of solution for the leveling additive.

The calibration matrix was set up using a regular measurement arrangement with a measurement cell, containing a triple-electrode arrangement (rotating platinum disk electrode as working electrode, platinum network as counter electrode and silver/silver chloride electrode (Ag/AgCl) as reference electrode), a commercial potentiostat with integrated function generator to produce a linear potential/time gradient and an evaluation unit with a

current/time integration module to find the amount of charge. Cyclic voltammograms were recorded with this measurement arrangement with a time-constant feed speed of 100 mV/sec. The potential of the working electrode was varied within a voltage range from 0.25 to +1.0 V vs. Ag/AgCl. The amount of copper dissolved by the working electrode during anode reflux in the potential range from 0 to +0.3 V vs. Ag/AgCl is characterized by integration of the flowing stripping current. The amount was calculated as the mean of several runs of the potential range, wherein the first run, beginning with a potential of 1.0 V vs. Ag/AgCl was not included in finding the mean.

The measured values obtained for the stripping charge Q_{total} [mC/cm^2] for certain bath compositions, expressed in [ml BA or BL/l] are given in a 3D graph in Figure 1. The absolute errors for the individual measured values are added as error columns.

After the calibration matrix is set up, the bath found in the production operation is studied. The first method used was based on determining the concentration of brightening additive in the bath in the first step and then deriving the concentration of basic leveler from the concentration found using the calibration matrix.

The concentration of brightening additive was found in the following way: The measuring cell of the electrochemical arrangement was equipped with a titration burette. The burette was filled with the brightening additive CUPRACID®. Then 50 ml of the production bath was put into the measuring cell of the electrochemical arrangement. A cyclic voltammogram was recorded and according to the method above, the amount of copper dissolved by the working electrode was found. A specific charge value of 48 mC/cm^2 was found. This measured value was needed to find the basic leveler from the calibration matrix after the concentration of brightening additive was determined.

To find the content of brightening additive in the production bath, 0.75 ml of basic leveler CUPRACID® BL was added to the solution ($\triangleq$ 15 ml/l). Then a cyclic voltammogram was recorded again, and the amount of copper dissolved by the working electrode was found by the method above. After this first measured value for the charge was found in the titration (15 mC/cm^2), the amount of copper dissolved as a function of the titer volume (Fig. 2) was entered on a graph, and 25 µl of the titer liquid was let out of the burette into the measuring cell ($\triangleq$ 0.5 ml/l). After that, the amount of copper dissolved was found again by the method described above, and the measured value obtained was entered on the graph (Fig. 2). After this process was repeated many times, the line shown in Fig. 2 was obtained, from which after extrapolation on the abscissa, the amount of the current content of brightening additive was obtained (x_{EZ} = 1 ml brightening additive CUPRACID® BL (GZ) in 1 liter of solution).

The concentration of basic leveler was then able to be found by a comparison of the concentration of

brightening additive in the production bath with the calibration matrix, by comparing the measured value for the unchanged production bath (48 mC/cm^2) obtained before adding the basic leveler to the measurement solution with the concentration value obtained from the analysis for the brightening additive. From the charge value of 48 mC/cm^2 and a concentration of 1 ml of brightening additive CUPRACID® BLA solution, a concentration of 10 ml basic leveler CUPRACID®BL in 1 liter of solution was derived.

Example 2

In a second example, the concentrations of brightening and leveling additives of another production bath with the inorganic components given in Example 1 was found in the corresponding concentrations by first determining the concentration of leveling additive by the electrochemical method described and then using the value found and the calibration matrix already set up in Example 1 to derive the content of brightening additive. It was not necessary to set up a new calibration matrix, since the same one could be used for the second experiment. So, the content of individual additives only had to be determined by titration.

50 ml of a so-called basic bath (production bath as in Example 1 without brightening and leveler additives) was placed in the measuring cell of the electrochemical device, the amount of charge was measured from the dissolution peak by the method described and entered on a graph as a measuring point (amount of dissolved copper as a function of titer volume; Fig. 3). The measurement conditions were the same as in Example 1.

Next, a sample of the basic bath was titrated in a first titration cycle with a standard solution, which contained the basic leveler CUPRACID® BL in a concentration of 10 ml/l. After each addition, the amount of charge was measured again at the dissolution peak. The falling line A obtained in Fig. 3 was obtained.

Next the measuring cell was emptied, cleaned and then refilled with 50 ml of another sample of basic bath. In the second titration cycle, this bath sample was now titrated with a sample of the production bath. After each addition of production bath to the basic bath sample, the amount of charge was measured at the dissolution peak. The values were in turn entered on the above-mentioned graph (Fig. 3). A falling line B was obtained again, but it did not coincide with the first line A obtained (entered on the abscissa in Fig. 3: ml standard solution/1 or ml of production bath/l).

From the graph obtained, the concentration of basic leveler was obtained by the following formula:

$$X_{EZ} = C_{EZ}\ a_o / a_s$$

Where

X_{EZ} = the concentration of basic leveler in the production bath being analyzed,

C_{EZ} = 10 ml of basic leveler CUPRACID® BLA solution (known concentration of basic leveler in standard solution).

a_o = rise in standard titration curve (amount of metal dissolved again after deposition, expressed as Q_{total} in [mC/cm^2] as function of the volume of standard solution added to the titration, expressed in [ml/l]), and

a_s = rise in analysis titration curve (amount of metal dissolved again after deposition, expressed as Q_{total} in [mC/cm^2] as a function of the volume of production bath being analyzed added to the titration, expressed in [ml/l].

The content of basic leveler CUPRACID® BL (BL)/l of production bath was calculated at 5 ml.

After that, the measurement cell was emptied again, cleaned and filled with 50 ml of a sample of production bath. A cyclic voltammogram was made again with this sample, and the amount of charge at the stripping peak was found. The value was 80 mC/cm^2.

The value found in determining the concentration of basic leveler (5 ml BL/l), along with the charge value (80 mC/cm^2) for the production bath sample, using the calibration matrix set up before, gave a derived concentration value of 2 ml of brightening additive CUPRACID® BL/liter of solution.

Example 3

Example 1 was repeated. But the measurement arrangement was changed. Instead of a rotating disk electrode, a non-rotating microelectrode was used. The microelectrode was melted in a glass tube as roughly 50 μm thick wire and the tip of the tube was ground in the usual way. When this electrode was immersed in a bath sample, only the basically circular cross section of the wire, with a diameter of roughly 50 μm, was in contact with the bath sample.

Without taking special precautions for the reproducibility of the current and charge measurements to suppress the disturbing mass transport phenomenon at the working electrode, the same results were able to be obtained as in Examples 1 and 2.

Example 4

Example 1 was repeated with a bath sample that had a different additive content. But instead of the rotating disk electrode, a quartz resonator was used as the working electrode. These types of quartz resonators, which are coated with metal on the front and back side for oscillation excitation, was obtained from KVG, a company in Neckarbischofsheim, Germany. The oscillation frequency of this quartz was roughly 5 MHz. A regular excitation circuit was used to excite the oscillation. These types of circuits are used, inter alia, to measure layer thickness in vaporization and are therefore known. Corresponding examples of applications from electrochemistry are also known. Please refer to the explanations of R. Schumacher in Angew. Chemie (ibid.) [Applied Chemistry] and other references in this publication to additional sources under the numbers [5 to 8 and 28] there.

The contact in contact with the solution on the quartz was also used as an electrical feed for the potentiostatic measurement arrangement.

The mass change in the quartz was recorded as a frequency change Δf_{total}. In this case, the quartz had an active surface of 0.5 square centimeters.

First, as in Example 1, the calibration matrix was found, but instead of the amounts of charge that can be found electrochemically during dissolution of copper, the dissolved mass was recorded via the frequency change in Hz. The matrix obtained was shown in Fig. 4.

After that, the concentrations of brightening additive and basic leveler were found. In a first experiment, the concentration of brightening additive was found experimentally by the method described in Example 1, where instead of measuring the amounts of charge, the frequency change was measured on the quartz resonator. The frequency shift Δf_{total} for the unchanged production bath was 700 Hz. The content of brightening additive CUPRACID® BL found was 1 ml/l of solution. Using the calibration matrix already set up, along with the frequency shift for the unchanged production bath sample, the content of basic leveler was then determined. One liter of solution contained 5 ml of basic leveler CUPRACID® BL.

Example 5

In a second experiment, the process was like the one in Example 2, where, in this case, the concentrations of additive in the bath sample used were changed again (basic bath as in Example 2). The concentrations of additive were found by experimentally determining the content of basic leveler and then deriving the content of brightening additive. The frequency shift Δf_{total} for the unchanged production bath was 1000 Hz. The concentration value found experimentally for the basic leveler CUPRACID® BL was 15 ml/liter of solution. From this value and the frequency

shift measured for the unchanged production bath sample, the value for the content of brightening additive CUPRACID® BL was found to be 2 ml/liter of solution.

Example 6

The concentrations of brightening and leveling additives in a galvanic copper bath with the following composition were found:

Cu^{2+} (as $CuSO_4 \cdot 5H_2O$)	19 g/l
concentrated H_2SO_4	196 g/l
Cl (as NaCl)	50 mg/l
in water	

First a calibration matrix was set up for the organic components of the bath using the method given in Example 1. The bath contains as organic components the disodium salt of di-(ω-sulfopropyl)-disulfide as a brightening additive and a polyglycol ether as a leveling additive.

After finding the calibration matrix, a bath used in production with the brightening and leveling additive was studied.

In the first cyclo-voltammetry analysis, as given in Example 1, the concentration of brightening additive in the bath was found, and then the concentration of leveling additive was derived from the concentration found using the calibration matrix. A solution was used for titration that contained a concentration of 5 mg/l of the brightening additive.

From the titration lines obtained, after extrapolation on the abscissa, the amount of the current content of brightening additive was (x_{EZ} = 1 mg/l).

The concentration of leveling additive could then be found in the way described above by comparing the concentration of brightening additive in the production bath to the calibration matrix. The concentration found for the leveling additive was 300 mg/l.

Example 7

In another example, the concentrations of brightening and leveling additive in the production bath given in Example 6 were found by the method given in Example 2. The content of leveling additive found was 3000 mg/l. The concentration of leveling additive, using the calibration matrix set up beforehand, gave a derived value for the concentration of brightening additive of 10 mg/l.

Patent Claims

1. A method for separate analytical determination of the concentrations of brightening and leveling additives in galvanic metal deposition baths, in which the potential of the working electrode versus the reference electrode is varied cyclically between potential limits in an electrochemical arrangement with working, counter and standard electrodes in a measurement cell, and in which for this

a. the metal deposition bath is transferred into the measurement cell,

b. the concentration of leveling additive is found by a titration method, by finding the amount of metal in each titration step that is deposited on the working electrode or is dissolved again after deposition, and in which

c. the concentration of brightening additive is then determined,

characterized by the fact that the concentration of brightening additive is derived from the concentration of leveling additive already found and the correlation between the amount of metal deposited on the working electrode or dissolved again after deposition in the composition of a metal deposition bath with known concentrations of brightening and leveling additives.

2. The method in Claims 1, characterized by the fact that the concentration of leveling additive in the metal deposition bath is found by titrating a metal deposition bath without additives in two titration phases

- once with the metal deposition bath being analyzed and
- once with a standard solution containing the leveling additive in a known concentration,

and the concentration of leveling additive is calculated using the equation

$$X_{EZ} = C_{EZ}\, a_u / a_s$$

where

X_{EZ} = the concentration of leveling additive in the metal deposition bath being analyzed,

C_{EZ} = the known concentration of leveling additive in standard solution

a_u = the rise in the titration analysis curve (amount of metal deposited or dissolved again after deposition as a function of the volume of the metal deposition bath being analyzed that was added during titration) and

a_s = the rise in the standard titration curve (amount of metal deposited or dissolved again after deposition as a function of the volume of standard solution added during titration).

3. The method of separate, analytical determination of the concentrations of brightening and leveling additives in galvanic metal deposition baths in which the potential of the working electrode versus the reference electrode is

varied cyclically between potential limits in an electrochemical arrangement with a working, counter and reference electrode in a measurement cell, and in which

a. the metal deposition bath is transferred into the measurement cell,

b. the concentration of brightening additive is found by a titration method, by finding the amount of metal in each titration step that is deposited on the working electrode or is dissolved again after deposition, and in which

c. the concentration of leveling additive is then determined,

characterized by the fact that the concentration of leveling additive is derived from the concentration of brightening additive already found and the correlation between the amount of metal deposited on the working electrode or dissolved again after deposition in the composition of a metal deposition bath with known concentrations of brightening and leveling additives.

4. The method in Claim 3, characterized by the fact that the concentration of brightening additive in the metal deposition bath is determined by titrating the metal deposition bath being analyzed with a standard solution containing a known concentration of brightening additive and deriving the concentration from the abscissa section of the titration curve obtained (quantity of metal deposited or dissolved again after deposition as a function of the volume of standard solution added to the titration).

5. The method in Claim 4, characterized by the fact that before titration of the metal deposition bath being analyzed with the standard solution, a fixed amount of leveling additive is added to the bath being analyzed.

6. The method in one of the preceding claims, characterized by the fact that the correlation between the amount of metal deposited on the working electrode or dissolved again after deposition and the composition of a metal deposition bath with known concentrations of brightening and leveling additives is determined in the following way:

a. Make metal deposition baths with known concentrations of brightening and leveling additives.

b. Determine the quantity of metal deposited on the working electrode or dissolved again after deposition with each of the metal deposition baths made.

c. Assign measured values for the amount of metal deposited on the working electrode or dissolved again after deposition to the predetermined pairs of concentration values for the brightening and leveling additives.

7. The method in one of the preceding claims, characterized by the fact that to determine the amount of metal deposited on the working electrode or dissolved again after deposition, the amount of charge is determined during deposition and/or subsequent dissolution of the metal by integrating the flowing current during deposition as it goes

through the deposition area and/or the flowing current during dissolution going through a current peak that occurs during dissolution.

8. The method in one of the preceding claims, characterized by the fact that the working electrode is designed as a microelectrode.

9. The method in Claim 8, characterized by the fact that the microelectrode in the cross section of a high-quality metal wire embedded in an insulating material with a diameter of 50 µm maximum is used.

10. The method in one of Claims 1 to 6, characterized by the fact that to determine the amount of metal deposited on the working electrode, a quartz resonator coupled to a suitable oscillation excitation circuit with an electrode surface as the working electrode is used, the frequency change during deposition and/or during dissolution of the metal is measured, and the amount of metal deposited and/or dissolved is determined from the frequency change by means of an experimentally determined calibration line or with the Sauerbrey equation and the Faraday equation.

11. The use of the method in one or the preceding claims to determine the concentrations of additives in galvanic copper deposition baths.

4 pages of drawings attached

Nummer: DE 199 11 447 A1
Int. Cl.⁷: G 01 N 31/02
Offenlegungstag: 7. Dezember 2000

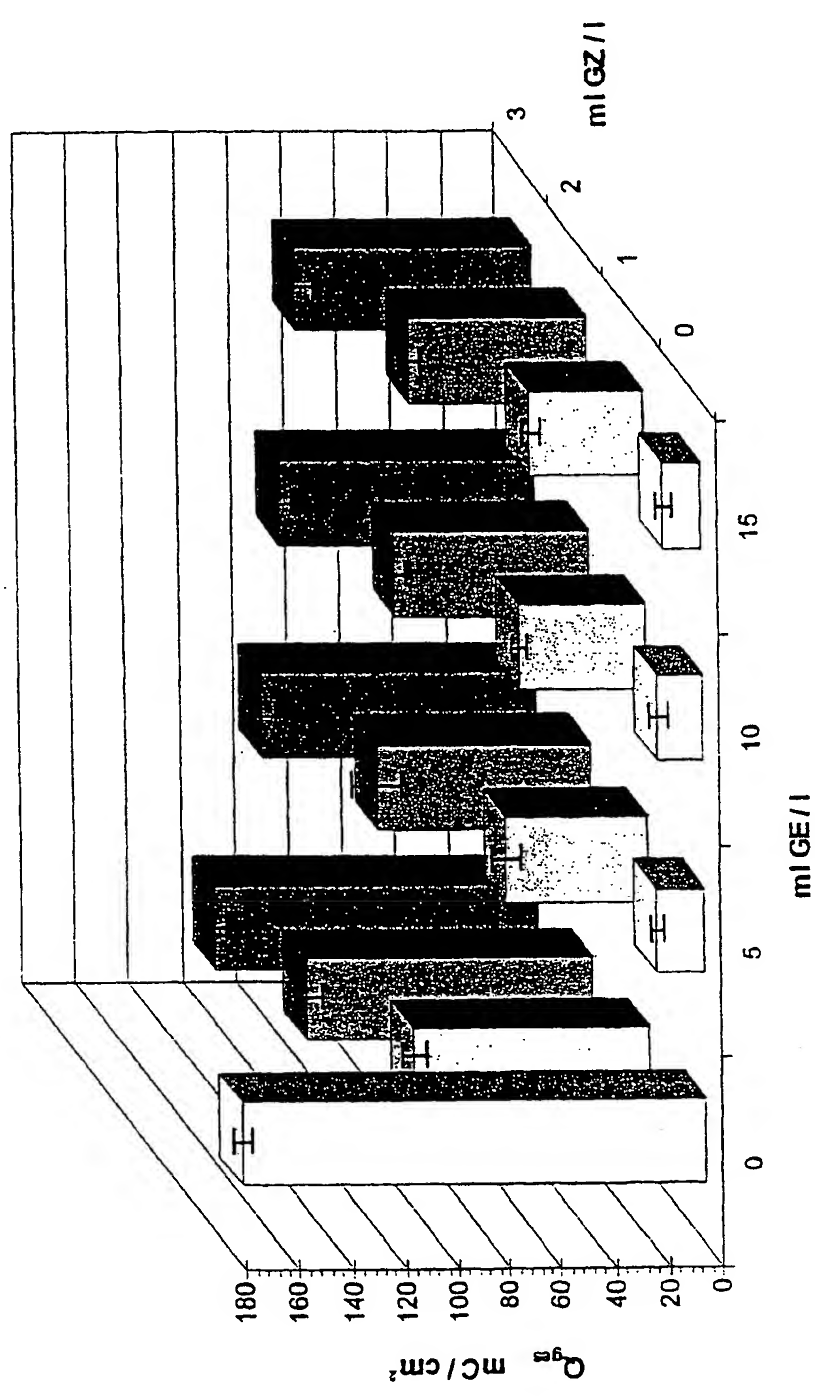

Fig. 1

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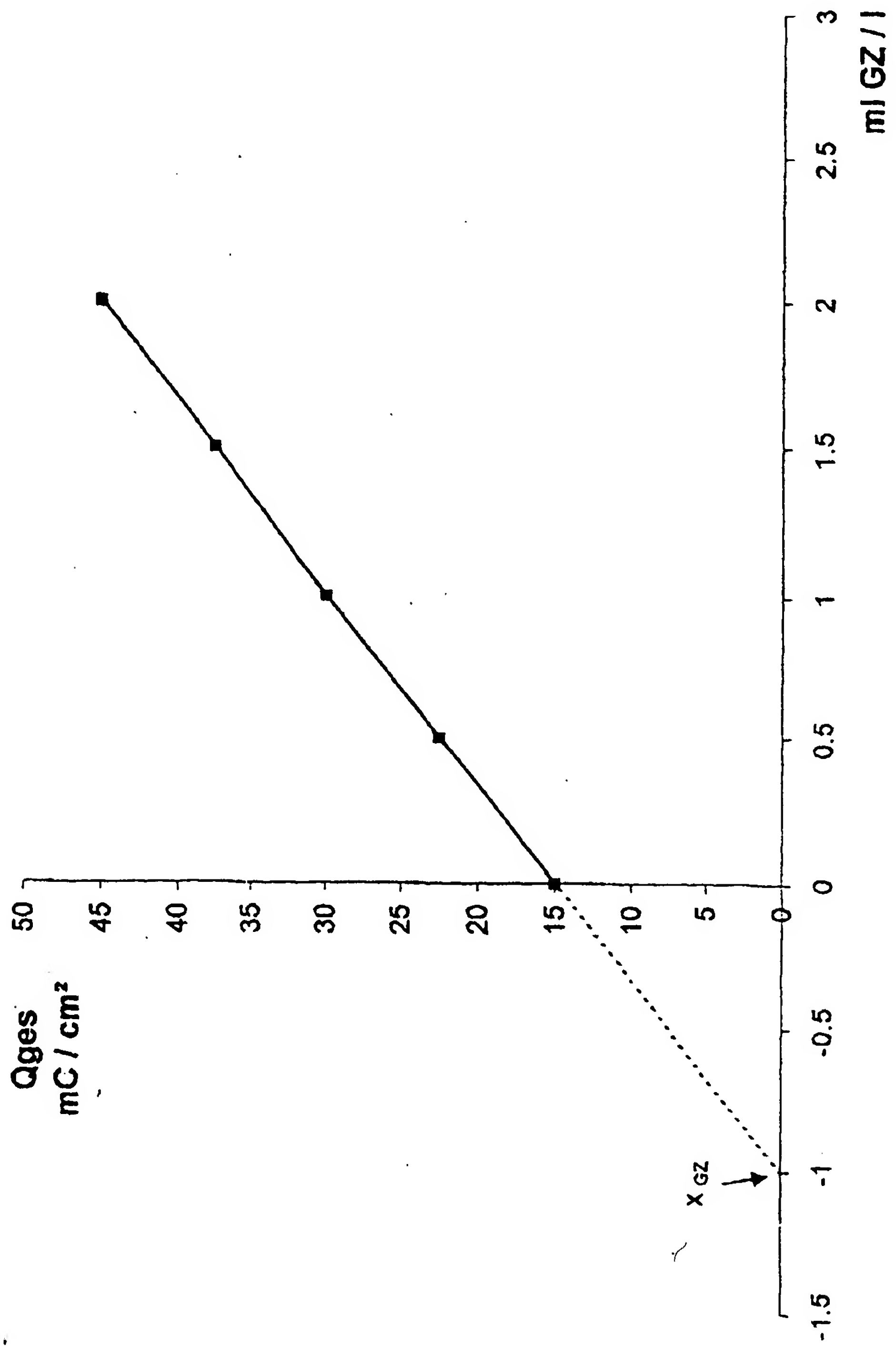

Fig. 2

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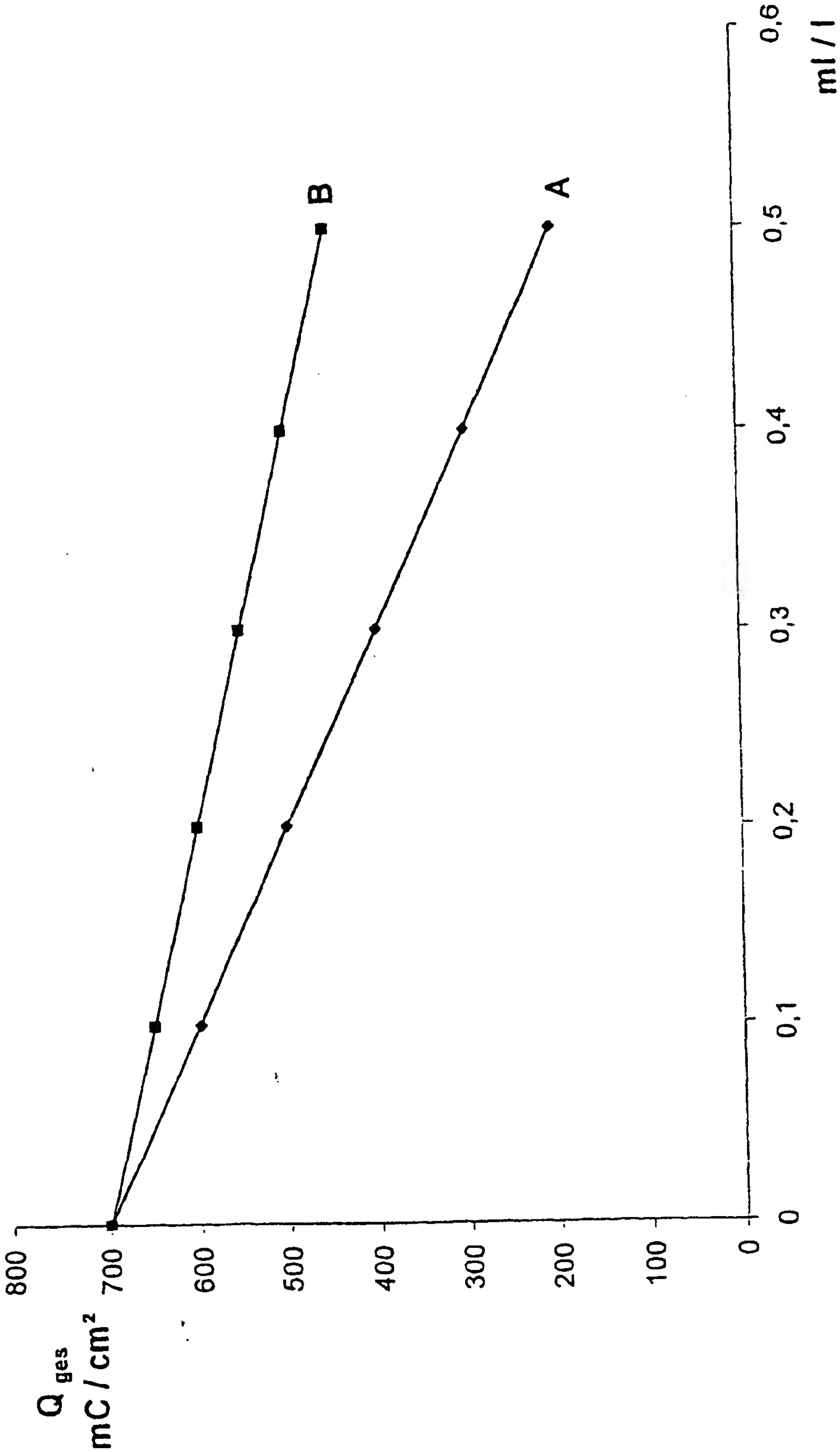

Fig. 3

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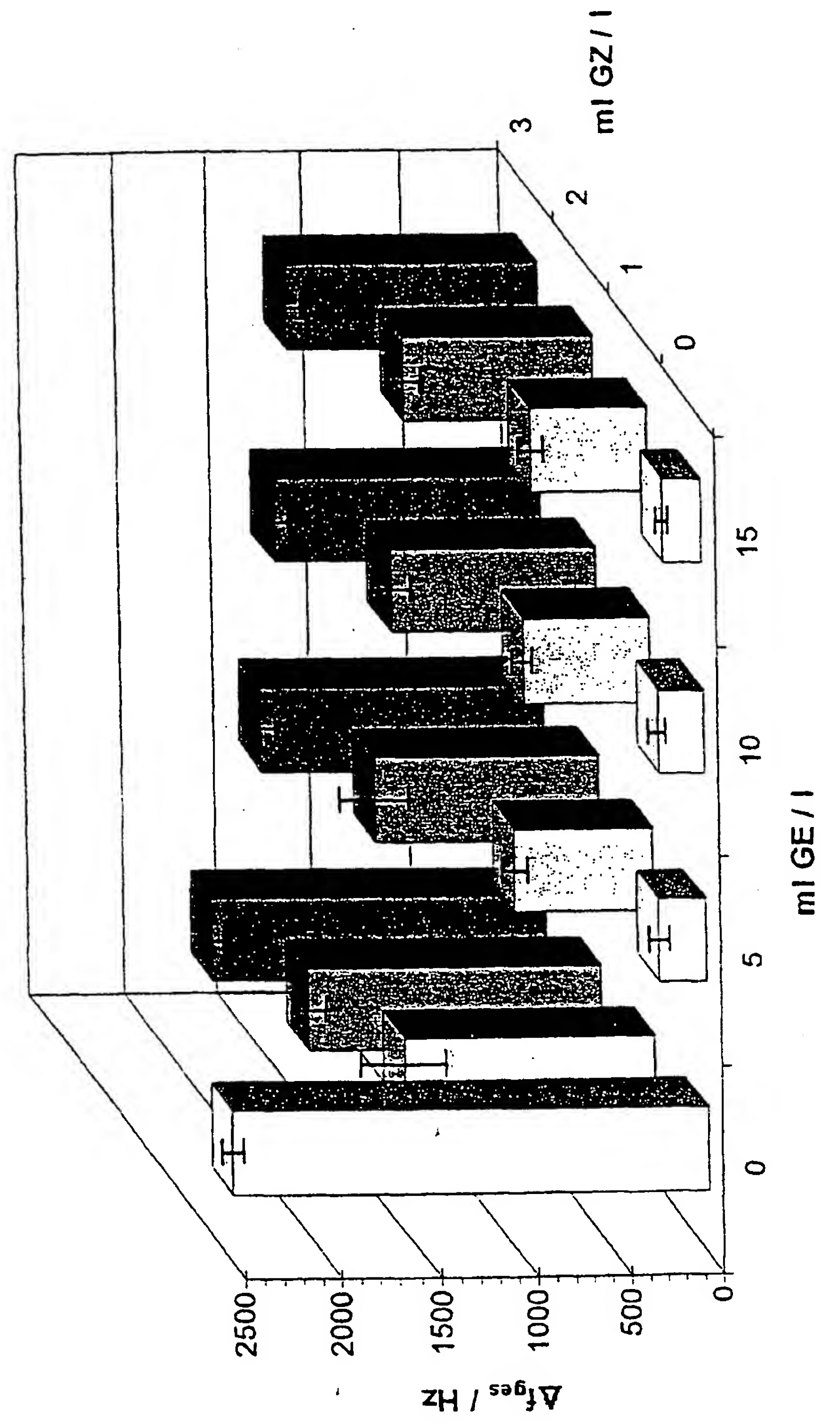

Fig. 4